PB84-110139

Experimental Protocol for Determining Protolysis Reaction Rate Constants

California Univ., Riverside

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Oct 83

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-83-100	2.
3. RECIPIENT'S ACCESSION NO. PB84 110139	
4. TITLE AND SUBTITLE EXPERIMENTAL PROTOCOL FOR DETERMINING PHOTOLYSIS REACTION RATE CONSTANTS	5. REPORT DATE October 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W.P.L. Carter, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr.	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Statewide Air Pollution Research Center University of California Riverside, California 92521	10. PROGRAM ELEMENT NO. CCUL1A-01 Task 0518 FY-83
	11. CONTRACT/GRANT NO. EPA-CR-806661
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environemtnal Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA-600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

An experimental protocol to determine photolysis rates of chemicals which photolyze relatively rapidly in the gas phase has been developed. This procedure provides a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e., photolysis) for organic substances which may be emitted into the environment and which strongly absorb actinic radiation and photodecompose with high efficiencies. This technique is based upon monitoring the disappearance rates of the test compound and of a reference organic, both of whose OH radical reaction rate constants are accurately known, in irradiated NO-organic-air mixtures. Depending on the reproducibility of the analysis technique, photolysis rates $\geq 1 \times 10^{-5}$ sec^{-1} can be determined using this technique. This limits the procedure to these organics which photolyze relatively rapidly, such as nitrites, α-dicarbonyls and nitrosamines. However, while the technique cannot be used for simple aldehydes and ketones and other relatively weakly absorbing organics, for most species this may not be a serious limitation because their atmospheric lifetimes are determined mainly by reaction with OH radicals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 49
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB84-110139

EPA-600/3-83-100
October 1983

EXPERIMENTAL PROTOCOL FOR DETERMINING PHOTOLYSIS REACTION RATE CONSTANTS

by

W. P. L. Carter, R. Atkinson, A. M. Winer and J. N. Pitts, Jr.

Statewide Air Pollution Research Center
University of California
Riverside, CA 92521

EPA Cooperative Agreement CR806661-01

Bruce W. Gay, Jr.
Environmental Sciences Research Laboratory
Research Triangle Park, NC 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

An experimental protocol for the determination of photolysis rates of chemicals which photolyze relatively rapidly in the gas phase at room temperature has been developed, and is described in detail. This procedure provides a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e., photolysis) for organic substances which may be emitted into the environment and which strongly absorb actinic radiation and photodecompose with high efficiencies. This technique is based upon monitoring the disappearance rates of the test compound and of a reference organic, both of whose OH radical reaction rate constants are accurately known, in irradiated NO-organic-air mixtures.

Irradiations employing blacklamps emitting in the actinic region are carried out in ~75-liter volume cylindrical Teflon bags. The concentrations of the reactants are: NO, ~5 ppm; test compound, ~1 ppm; reference organic, ~1 ppm. The test compound and reference organic are monitored by gas chromatography; NO, NO_x and O_3 are monitored by chemiluminescence. The light intensity in the experimental system is monitored by NO_2 actinometry, and corrections for the differences in light intensity between the experimental system and the atmosphere are made by multiplying the measured photolysis rate of the test compound by the ratio of the calculated atmospheric photolysis rate to the measured laboratory NO_2 photolysis rate.

Ideally, the light source in the chamber should have the same spectral distribution and intensity as solar radiation at the earth's surface at the appropriate latitude. Unfortunately, practical limitations (i.e., cost and complexity) dictate the use of blacklamps, the type typically used in environmental chamber studies of the photooxidations of organics. The fact that the spectral distribution provided by these lamps is different from the solar spectral distribution leads to uncertainties when extrapolating the chamber results to ambient conditions.

Depending on the reproducibility of the analysis technique, it is anticipated that photolysis rates $\gtrsim 1 \times 10^{-5}$ sec^{-1} in the chamber can be determined using this technique. This limits the procedure to these organics which photolyze relatively rapidly, such as nitrites, α-dicarbonyls and nitrosamines. However, while the technique cannot be used for

simple aldehydes and ketones and other relatively weakly absorbing organics, for most species this may not be a serious limitation because their atmospheric lifetimes are determined mainly by reaction with OH radicals.

CONTENTS

Abstract		iii
Figures		vii
Tables		viii
I.	Introduction and Background	1
	A. General Approach Employed	3
	1. Laboratory Measurement of Photolysis Rates	4
	2. Laboratory Measurement of the NO_2 Photolysis Rate	6
	3. Estimation of the Tropospheric Photolysis Rate of the Test Compound	7
	B. Limitations and Uncertainties	8
	1. Minimum Measurable Photolysis Rates	8
	2. Uncharacterized Loss Processes Affecting Photolysis Rate Measurements	9
	3. Application of Experimentally Measured Photolysis Rates to Photolysis in the Troposphere	10
II.	General Equipment and Materials Required	14
	A. Methods for the Analyses of the Test and Reference Organics	14
	B. Ozone Monitor	15
	C. NO-NO_2-NO_x Monitor	15
	D. Reaction Chamber and Fluorescent Lamp Irradiation Assembly	15
	1. Reaction Chamber	15
	2. Injection and Sampling Port	16
	3. Heat Sealing	16
	4. Reaction Bag Cover	16
	5. Seal Reinforcement and Leak Testing	19

6. Fluorescent Lamp Assembly 19

E. Reactor and Associated Apparatus for NO_2 Actinometry 19

F. Flowmeter 22

1. Range and Application 22

2. Calibration of the Rotameter 22

III. Experimental Protocol 25

A. Experimental Procedure for the Determination of Rate Constants for Photolysis 25

1. Filling the Reaction Bag 25

(a) Injection of Test Compound and Reference Organic 25

1. Gaseous Compounds 25

2. Liquid Compound 27

(b) Injection of NO 29

2. Procedure for Photolysis Experiment 29

B. Choice of Reference Organic 30

C. Experimental Procedure for Measurement of the NO_2 Photolysis Rate 31

D. Determination of the Dark Decay Rate of the Test Organic 32

E. Tests of the Experimental Technique and Potential Problem Areas 33

F. Data Analysis 34

G. Information to be Reported 36

References 38

FIGURES

Number		Page
1	Relative Spectral Distributions for the Blacklamps and the Solar Spectrum, Normalized to the Same NO_2 Photolysis Rate	11
2	Construction of the Teflon Reaction Bag	17
3	Injection and Sampling Port	18
4	Fluorescent Lamp Assembly	20
5	Schematic of NO_2 Actinometry Apparatus	21
6	Design of a Bubble Flowmeter	23
7	Syringe-to-Syringe Gas Transfer	26
8	Design of Pyrex Bulb for Injection of Gaseous or Liquid Compounds	28

TABLES

Number		Page
1	Calculated Tropospheric Photolysis Rates for NO_2 as a Function of Solar Zenith Angle	8
2	Errors in Estimating Tropospheric Photolysis Rates from Photolysis Rates Measured Using Blacklight Irradiations for Selected Photolysis Reactions	13
3	List of Reference Organics for which Accurate OH Radical and O_3 Reaction Rate Constants are Available and which do not Photolyze	32

SECTION I

INTRODUCTION AND BACKGROUND

Chemical compounds emitted into the atmosphere are removed by several pathways, including degradation by chemical reaction or wet or dry deposition. Laboratory and environmental chamber studies have shown that for the ambient atmosphere the following gas phase removal routes are likely to be important (see, for example, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Atkinson et al. 1979, Atkinson and Lloyd 1983 and references therein):

- Reaction with the hydroxyl (OH) radical
- Reaction with ozone (O_3)
- Photolysis, which involves absorption of light followed by isomerization or decomposition
- For aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO_3) radical.

Hence, in order to assess (a) the atmospheric lifetime of compounds with respect to these gas-phase removal processes and (b) the relative importance of each of these reaction pathways, rate constants for photolysis and/or chemical reaction must be experimentally determined for individual compounds.

Experimental protocols for determination of rate constants for the reaction of organics with ozone (Pitts et al. 1981a) and for reactions of organics with hydroxyl radicals (Pitts et al. 1982) are described elsewhere. Also available (Pitts et al. 1981b) is an experimental protocol for determination of absorption cross-sections of organics, from which upper limit photolysis rates can be calculated.

In this document, an experimental protocol for measuring the rates of photolysis of organics under conditions approximating those of the atmosphere is described. Due to experimental limitations, this protocol is

applicable only for organics which photolyze relatively rapidly (lifetimes of $\lesssim$ 30 hrs). These include strongly absorbing species which photodissociate rapidly, such as nitrites, α-dicarbonyls and nitrosamines. Fortunately, most organics which photolyze also react rapidly with the hydroxyl radical, so for these compounds this shortcoming is not overly serious in terms of estimating atmospheric lifetimes. However, there are a few organics (e.g., acetone, methyl ethyl ketone and diethyl ketone) which react only slowly with OH radicals and do not react with O_3, and which photolyze at rates lower than the range for which this protocol is useful; for these compounds alternate techniques for determining photolytic lifetimes are required.

Under atmospheric conditions, the photolysis rate constant, k_p, for the reaction

$$\text{test compound} + h\nu \rightarrow \text{products} \qquad (1)$$

is given by

$$k_p = \int_{290\ \text{nm}}^{800} \sigma_\lambda \phi_\lambda J_\lambda d\lambda \qquad (I)$$

where σ_λ is the absorption cross-section at the wavelength λ, ϕ_λ is the corresponding quantum yield (the fraction of molecules absorbing light which subsequently isomerize or decompose; always $\leq$ 1.00 for elementary reactions), and J_λ is the solar flux at the wavelength λ.

The short wavelength cut-off of $\lambda \simeq 290$ nm is determined by the transmission properties of the atmosphere (Peterson 1976, Demerjian et al. 1980), while the long wavelength limit is set by thermochemistry, since light of wavelength > 800 nm is not of sufficient energy to break chemical bonds of ground state, thermally stable molecules (Calvert and Pitts 1966, Benson 1976). The solar flux is conveniently tabulated as average values of $J_{\Delta\lambda}$ over 10 nm intervals, so the integral in equation (I) can be replaced by a summation to yield

$$k_p = \sum_{\lambda=290\ \text{nm}}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda} \phi_{\Delta\lambda} \qquad (II)$$

where $\sigma_{\Delta\lambda}$ and $\phi_{\Delta\lambda}$ also represent the absorption cross-section and quantum yield values averaged over 10 nm intervals. Tabulated values of $J_{\Delta\lambda}$ for various latitudes and various times are given elsewhere (Peterson 1976, Hendry and Kenley 1979, Pitts et al. 1981b).

Thus from a knowlege of the absorption coefficients $\sigma_{\Delta\lambda}$ of the organic of interest, the quantum yields $\phi_{\Delta\lambda}$ for photolysis reactions which lead to its removal, and with the tabulated values of $J_{\Delta\lambda}$, the photolysis rate constant k_p can in principle be calculated for any latitude, season, and time of day without the necessity for experimental rate measures. However, the accurate determination of quantum yields for organic compounds in air as a function of wavelength is a highly complex and time-consuming proposition, and the routine determination of absolute quantum yields is not practical at the present time. On the other hand, a relatively straightforward experimental protocol is available for the measurement of absorption coefficients of organics (Pitts et al. 1981b). Since quantum yields for elementary photochemical reactions cannot exceed unity, then upper limits to the atmospheric photolysis rate constants can be estimated, on the assumption that $\phi_\lambda = 1.00$

$$k_p^{max} = \sum_{\lambda=290}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda} \qquad \text{(III)}$$

This approach, which is described in detail elsewhere (Pitts et al. 1981b), is useful for determining the organics for which atmospheric removal by photolysis is not important. However, for those organics whose maximum photolysis rate is significant, a more quantitative indication of the actual tropospheric photolysis rates must also be obtained experimentally.

A. General Approach Employed

The approach described in this document for obtaining estimates for atmospheric photolysis rates for organics consists of (1) experimentally measuring in the laboratory the photolysis rate (or its upper limit) of the organic in air, employing a light source whose intensity and spectral distribution approximates as closely as practical that of the troposphere; (2) measuring the rate of NO_2 photolysis upon irradiation with the same light source and the same intensity as used in the organic photolysis rate

measurements; and (3) estimating the photolysis rate of the organic in the troposphere from the known tropospheric NO_2 photolysis rates (Demerjian et al. 1980) based on the assumption that the NO_2/organic photolysis rate ratios is the same in the experimental system as in the troposphere. This approach involves a number of assumptions which may not always be valid; the uncertainties and limitations involved are discussed in Section I B.

1. Laboratory Measurement of Photolysis Rates

The experimental approach for the laboratory measurement of the photolysis rate of the organic test compound is based on measuring the disappearance rates of that compound and of a reference organic in irradiated NO-test compound-reference organic-air mixtures, where conditions are such that the major loss processes for the test compound should only be photolysis and perhaps reaction with the hydroxyl radical. The reference organic is chosen to be a compound which does not photolyze and whose major loss process in such systems is reaction with the hydroxyl radical, preferably with a rate constant similar to that of the test compound. The NO levels employed are sufficiently high that the concentrations of O_3 and NO_3 are suppressed, so that reaction of the organics with these species is minimized.

Thus the reactions which must be considered in the NO-organic-air system used to determine photolysis rates are those listed below:

$$\text{test compound} + h\nu \xrightarrow{k_p} \text{products} \qquad (1)$$

$$\text{test compound} + OH \xrightarrow{k_2} \text{products} \qquad (2)$$

$$\text{test compound} + \text{wall} \xrightarrow{k_3} \text{loss of test compound} \qquad (3)$$

$$\text{reference organic} + OH \xrightarrow{k_4} \text{products} \qquad (4)$$

Note that in practice, for a test compound whose behavior in the gas phase may not be well characterized, the possibility of heterogeneous removal (reaction 3) must be considered. Based on the above reactions, we can derive:

$$-d\ln[\text{test compound}]/dt = k_2[OH] + k_p + k_3 \qquad (IV)$$

and

$$-d\ln [\text{reference organic}]/dt = k_4[OH] \qquad (V)$$

and hence,

$$\frac{1}{(t-t_o)} \ln \left\{ \frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t} \right\} = \frac{1}{(t-t_o)} \frac{k_2}{k_4} \ln \left\{ \frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t} \right\} + (k_p + k_3) \qquad (VI)$$

where t_o is the time of the beginning of the irradiation and t is any time during the irradiation when both the test and reference compounds were measured. Thus a plot of $\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against $\ln([\text{reference organic}]_{to}/[\text{reference organic}]_t)$ should yield a straight line plot with an intercept of $(k_p + k_3)$ or, alternatively, since the rate constant ratio k_2/k_4 will be known, values of $(k_p + k_3)$ can be calculated from the experimental data and equation (IV). If reaction (3) is assumed to be primarily dark decay, k_3 can be measured by monitoring the rate of decay of the test compound in the dark, allowing k_p in principle to be calculated.

As indicated above, the formation of ozone should be minimized in this system, since certain organics (e.g., alkenes and other unsaturated compounds) react at significant rates with O_3, and others (e.g., phenols) react significantly with NO_3 radicals which are formed from the reaction of O_3 with NO_2. Since the OH radical and O_3 reaction rate constants for the test compound will have been determined as described by Pitts et al. (1981a, 1982), the importance of reaction with O_3 can readily be calculated, since

$$\frac{O_3 \text{ reaction}}{\text{OH radical reaction}} = \frac{k^{O_3}[O_3]}{k_2[OH]} \qquad (VII)$$

where k^{O_3} is the rate constant for the reaction of the test compound with O_3. The average OH radical concentration during a given irradiation period (times t_1 to t_2) can be determined from the rate of decay of the reference organic using equation (VIII):

$$[OH]_{avg} = \frac{\ln([\text{reference organic}]_{t_1} / [\text{reference organic}]_{t_2})}{k_4 (t_2 - t_1)} \qquad \text{(VIII)}$$

where k_4 is the rate constant for the reaction of OH radicals with the reference organic (reaction 4). Under conditions where [NO] $\gg$ [NO_2], the ozone concentration is usually not measurable, but can be estimated using the following steady-state equation:

$$[O_3] \simeq \frac{k^{lab}_{NO_2}}{k_{O_3+NO}} \frac{[NO_2]}{[NO]} \qquad \text{(IX)}$$

where $k^{lab}_{NO_2}$ is the measured NO_2 photolysis rate in the laboratory system (see following section), and k_{O_3+NO} is the known (Atkinson and Lloyd 1983) rate constant for the rapid reaction of O_3 with NO. Data obtained under conditions where the rate of consumption of the test compound (or reference organic) by reaction with O_3 becomes $\gtrsim$ 10% of the rate of consumption by reaction with OH radicals [as calculated from equation (VII)] should be neglected in the subsequent data analysis.

2. Laboratory Measurement of the NO_2 Photolysis Rate

The experimental approach for measuring the rate of photolysis of NO_2 in the laboratory system ($k^{lab}_{NO_2}$) is based on measuring the amount of NO_2 converted to NO when an NO_2 in N_2 mixture is irradiated while passing through a quartz tube at a known flow rate (Zafonte et al. 1977). The experimental NO_2 photolysis rate, $k^{lab}_{NO_2}$, is given by

$$k^{lab}_{NO_2} = \frac{\Delta[NO]}{[NO_2]} \cdot \frac{F}{V} \cdot \frac{1}{\Phi} \qquad \text{(X)}$$

where Δ[NO] is the measured increase in the NO concentration resulting from photolysis, [NO_2] is the NO_2 concentration in the tube, F is the total flow rate through the tube (generally ~3 liter min^{-1}), V is the volume of the portion of the tube exposed to the photolyzing light, and Φ is the effective quantum yield for the net production of nitric oxide upon photolysis. This effective quantum yield was calculated by Zafonte et al.

(1977) to be 1.61 ± 0.07 under the range of reactant concentrations generally employed ($[NO_2] \cong$ 1-4 ppm; $[NO]_o \cong$ 0-0.3 ppm). Zafonte et al. (1977) also calculated that no correction for refraction of light through quartz is necessary when a tubular reactor is employed.

3. Estimation of the Tropospheric Photolysis Rate of the Test Compound

The tropospheric photolysis rate of NO_2 ($k_{NO_2}^{trop}$) can be calculated as a function of the solar zenith angle, Z, from tabulated solar fluxes, $J_\lambda^{trop}(Z)$ and the known NO_2 absorption coefficients, $\sigma_\lambda^{NO_2}$ and photodecomposition quantum yields, $\Phi_\lambda^{NO_2}$, using the equation

$$k_{NO_2}^{trop}(Z) = \int_{\lambda=290}^{430} J_\lambda^{trop}(Z)\ \sigma_\lambda^{NO_2}\ \Phi_\lambda^{NO_2}\ d_\lambda \qquad \text{(XI)}$$

and representative values are tabulated in Table 1. The solar zenith angle depends on the time of day, the latitude, and the time of the year, and can be calculated as shown below:

$$Z = \arccos[\sin(L).\sin(D)-\cos(L).\cos(D).\cos(H)] \qquad \text{(XII)}$$

where

$$H = \left(\frac{\text{hours from midnight}}{24}\right) \times 360 \text{ degrees}$$

L = the latitude, and D = the solar declination angle at the time of year of interest (which can be obtained, for example, from a nautical almanac).

The ratio of the tropospheric to the laboratory measured NO_2 photolysis rates can then be used to obtain an approximate estimate of the tropospheric photolysis rate, k_p^{trop}, of the organic test compound from the photolysis rate measured in the laboratory:

$$k_p^{trop} \cong k_p^{lab}\ \frac{k_{NO_2}^{trop}}{k_{NO_2}^{lab}} \qquad \text{(XIII)}$$

Table 1. Calculated[a] Tropospheric Photolysis Rate for NO_2 as a Function of Solar Zenith Angle

Zenith Angle (deg)	$k_{NO_2}^{trop}$ (min^{-1})	Zenith Angle (deg)	$k_{NO_2}^{trop}$ (min^{-1})
0	0.464	45	0.375
5	0.463	50	0.350
10	0.460	55	0.319
15	0.455	60	0.282
20	0.448	65	0.239
25	0.439	70	0.187
30	0.428	75	0.129
35	0.414	80	0.070
40	0.396	85	0.025

[a]Calculated using the solar actinic fluxes given by Peterson (1976) based on his "best estimate" surface albidos, and the currently accepted values of the absorption coefficients and photodecomposition quantum yields for NO_2 (Atkinson and Lloyd 1983).

The validity of equation (XIII) critically depends on how closely the spectral distribution of the photolyzing light in the laboratory system approximates that of the troposphere; this is discussed in the following section.

B. Limitations and Uncertainties

1. Minimum Measurable Photolysis Rates

The minimum photolysis rate constant which can be measured using the technique described here depends on the precision and reproducibility of the gas chromatographic analysis of the test compound and the reference organic. Based on our experience with the proposed experimental system, it is anticipated that the photolysis rate constants must be at least ~1 x 10^{-5} sec^{-1} in order to be measurable. Thus this technique is only useful for organics which are highly photoreactive (much more so than, for example, simple aldehydes and ketones), and should not be attempted for organics whose value of k_p^{max}, calculated from the measured absorption

coefficients (Pitts et al. 1981b) using equation (III), is less than 10^{-5} sec^{-1}.

2. Uncharacterized Loss Processes Affecting Photolysis Rate Measurements

The proposed technique for the experimental measurement of photolysis rates is valid only if there are no significant loss processes for the test and reference organics in organic-NO_x-air irradiations other than reactions (1)-(4) discussed above. Of particular concern are (a) possible other gas phase reactions of the test compound, whose chemistry in irradiated NO_x-air systems in general may be highly uncertain, and (b) the possibility of light-induced first order wall losses of the organics. Both of these possibilities can be checked to some extent, but cannot be entirely ruled out. This means that the photolysis rates determined using this technique must always be considered to be upper limits.

An immediate indication of consumption of the test compound by some unsuspected bimolecular reaction with reactive intermediates or products formed in organic-NO_x-air irradiations will be obtained if plots based on equation (VI) are non-linear. However, linearity of plots of equation (VI) does not imply that such a reaction does not occur. The organic may be reacting with some species which does not change significantly in concentration during the irradiation, and thus a bimolecular removal process may appear to be first order. This possiblity can be checked, though not entirely ruled out, by varying the initial reactant concentrations to see if that affects the apparent photolysis rates. If the results of these experiments indicate such an unknown bimolecular removal process is important for a given test compound, the possibility that this process may be an important atmospheric sink for the test compound must be investigated. A discussion of the techniques for such investigations is beyond the scope of this document.

In practice we find that a more likely problem with the proposed technique may be first order, light-induced wall losses. In particular, anomolously high apparent photolysis rates for ketones (Atkinson et al. 1982a) and organic nitrates (Atkinson et al. 1982b) were determined using this technique. The possibility of light-induced wall losses of the reference organic can be tested in separate experiments by irradiating two different reference organics, which are known not to photolyze and which

have widely different OH radical rate constants, to see if one had a significantly (i.e., outside of two standard deviations) non-zero intercept in plots of equation (VI). If a non-zero intercept is observed, either another reference organic should be employed, or the reactor (which is a replaceable Teflon bag) should be changed. However, such a test cannot rule out light-induced wall decay of the test compound; the only test for this would be to determine if the apparent photolysis rate of the test compound changes when the reactor is changed.

3. Application of Experimentally Measured Photolysis Rates to Photolysis in the Troposphere

Equation (XIII), which relates the experimentally measured upper-limit photolysis rates to those appropriate to tropospheric conditions, is in general, as noted above, valid only if the spectral distribution of the light source employed in the laboratory is the same as that in the troposphere. Ideally, the best light source to use for the photolysis rate measurements would be natural sunlight. Indeed the protocol described in this document could be easily modified to use sunlight irradiation. However, an experimental protocol based on sunlight irradiation is not practical for routine use in most areas of the country.

The experimental protocol for determining photolysis rates in the laboratory which is described in this document is based on employing blacklight irradiation. Blacklights were chosen because they are relatively inexpensive and simple to use and because their short wavelength cut-off is reasonably close to that of the troposphere. However, their spectral distribution is significantly different than that of tropospheric sunlight, and thus they cannot be considered ideal for this purpose. A detailed consideration of the various possible light sources (or combinations thereof) which can be used in the laboratory is unfortunately beyond the scope of this document, and should be the subject of further investigation. In the subsequent discussion we will consider only the errors introduced by using blacklight irradiation. A similar analysis can be done with any other light source whose spectral distribution is known.

Figure 1 gives plots of the relative spectral distribution, for $\lambda \leq$ 500 nm, of blacklights of the type described in Section II, compared with those for tropospheric sunlight at three different Zenith angles. For the purposes of comparing relative distributions (as opposed to absolute

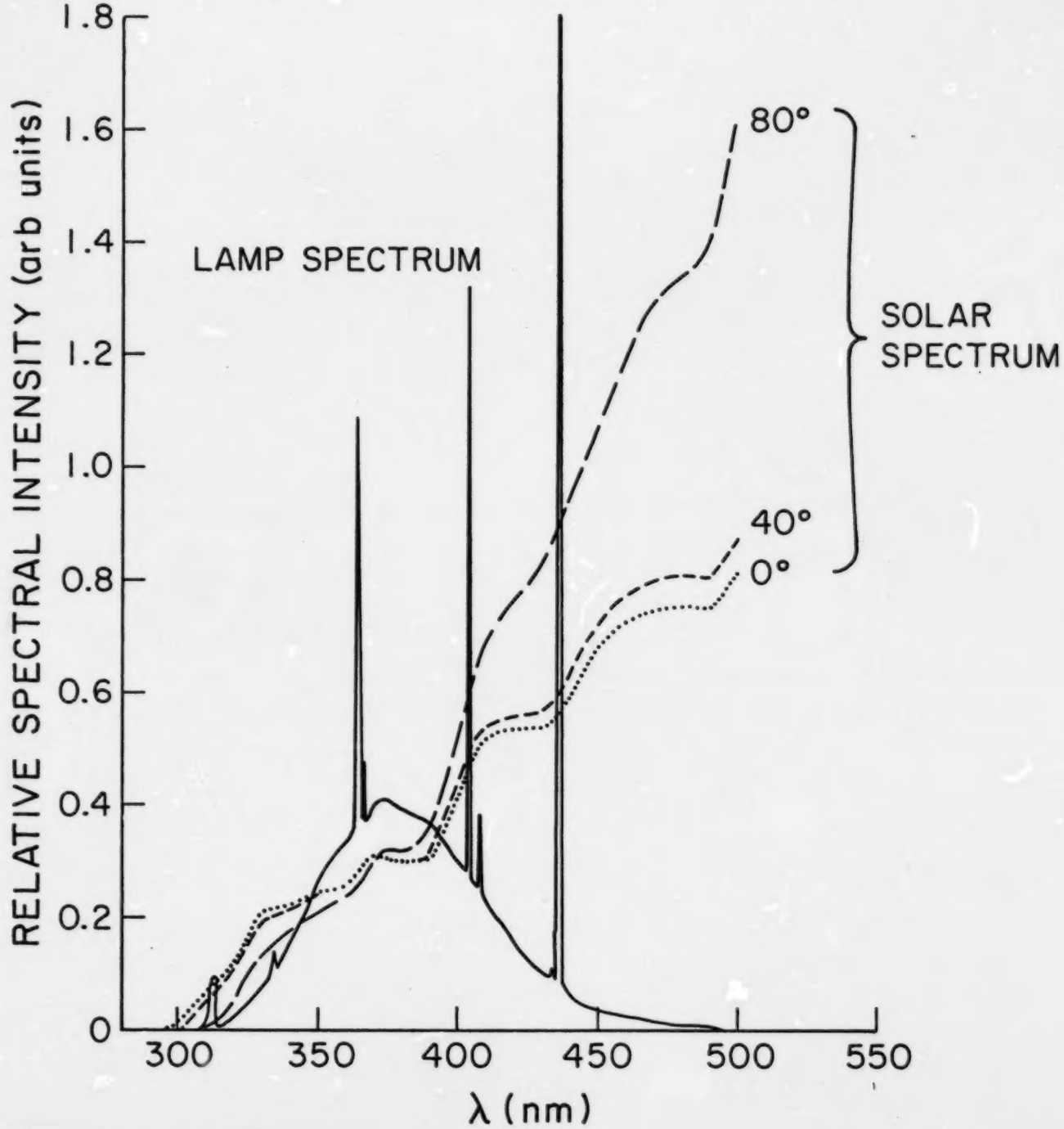


Figure 1. Relative Spectral Distributions for the Blacklamps and the Solar Spectrum, Normalized to the Same NO_2 Photolysis Rate

intensity), all curves shown in Figure 1 are normalized to give the same NO_2 photolysis rate. It can be seen that the blacklight spectral distribution is not a particularly good approximation of those of tropospheric sunlight, especially at $\lambda \gtrsim 400$ nm, where the blacklights are decreasing in intensity with wavelength, while sunlight is increasing in intensity. In particular, from Figure 1 it can be seen that if the compound photolyzes mainly below 345 nm, its tropospheric photolysis rate estimated from its photolysis rate in blacklight systems using equation (XI) would be low; if it photolyzes mainly in the wavelength region 345-390 nm the estimated photolyses rates would be somewhat high, while if it photolyzes in the wavelength region $\lambda \gtrsim 380$ nm, the estimated tropospheric photolysis rate would be low. Clearly blacklight irradiation is not suitable for compounds which photolyze primarily in the wavelength $\lambda \gtrsim 400$ nm.

The magnitude of the errors in estimated tropospheric photolysis rates based on blacklight photolysis rates for several representative photoreactive compounds is indicated in Table 2. The photolysis rates are calculated using the currently accepted absorption coefficients and quantum yields (Atkinson and Lloyd 1983), the tropospheric solar spectral distributions for overhead sun (Z = 0), and the blacklight spectral distributions. The wavelength regions of importance for the various photodecomposition processes shown are also given in Table 2. In general, it can be seen that, except for predictions of summer photolysis rates of compounds which photolyze primarily at the short wavelength cut-off (most of whose photolysis rate would probably be too low to measure experimentally in any case), the error introduced by using blacklight irradiation is usually on the order of a factor of two or less.

Table 2. The Effect of Estimating Tropospheric Photolysis Rates from Photolysis Rates Measured Using Blacklight Irradiations for Selected Photolysis Reactions.

Reaction[a]	Approx. Photolysis Spectral Region (nm)	Photolysis Rate (10^{-5} sec^{-1})		
		Calculated Solar Z = 0	Estimated Equation (XIII)	Est./Calc.
$O_3 + h\nu \rightarrow O(^1D) + O_2$	<320	8.5	0.36	0.04
$H_2O_2 + h\nu \rightarrow 2\ OH$	<340	1.18	0.48	0.41
$CH_3CHO + h\nu \rightarrow CH_3 + CHO$	<335	0.69	0.092	0.13
$C_2H_5\overset{O}{\overset{\|}{C}}CH_3 + h\nu \rightarrow C_2H_5 + CH_3CO$[b]	<340	1.99	0.36	0.18
$CH_3ONO + h\nu \rightarrow CH_3O + NO$[b]	<410	217	217	1.00
$(CH_3)_2N\text{-}NO + h\nu \rightarrow (CH_3)_2N + NO$[b,c]	~310-420	246	296	1.20
$HC\overset{OO}{\overset{\|\|}{C}}CH + h\nu \rightarrow$ products[b,c]	<465	226	170	0.75
$CH_3C\overset{OO}{\overset{\|\|}{C}}CH_3 + h\nu \rightarrow$ products[b,d]	<470	170	82	0.48

[a]Except as noted, absorption coefficients and quantum yields used were those recommended by Atkinson and Lloyd (1983).
[b]Calculated assuming quantum yields = 1 at all wavelengths.
[c]Absorption coefficients from Lindley (1979).
[d]Absorption coefficients from Plum et al. (1983).

SECTION II

GENERAL EQUIPMENT AND MATERIALS REQUIRED

To determine rates of photolysis of organics using the method outlined above, the following major equipment is needed:

- Gas chromatographs for the analysis of the test and reference organics
- An ozone monitor equipped with a filter to remove particulates
- An NO-NO_2-NO_x-monitor
- A Teflon bag or chamber in which the reaction can be carried out
- An arrangement of fluorescent lamps
- A quartz flow tube

The specific requirements and recommendations for these items of equipment are discussed below.

A. Methods for the Analyses of the Test and Reference Organics

While it can be seen [equation (VI)] that only relative measurements of the test and reference organic concentrations are necessary, it is recommended that quantitative analyses be carried out. For the development of this experimental protocol, gas chromatography has been used to analyze the test and reference organics. However, any analysis technique that is specific for the test and reference organics and which samples over a short time period compared to the irradiation times can in principle be used (e.g., mass spectrometry, combined gas chromatography-mass spectrometry and spectroscopic techniques). Since sampling for the test and reference organics must be carried out simultaneously for this protocol, the same technique of choice should be used in both cases. It is taken for granted that quantitative analyses of the test compound by such techniques at the concentrations necessary for this protocol (i.e., ~0.1-1 ppm) will have been developed by the chemical manufacturer, since this aspect of the protocol is beyond the scope of this document.

For the reference organics which are recommended for use here (see Section III.F), the gas chromatographic columns and conditions used in the development of this protocol were as follows (Pitts et al 1979):

n-Butane, cyclohexane, isoprene and 2-methyl-2-butene (and other C_4 through C_{10} n-alkanes) were analyzed using a 20 ft x 1/8 in stainless

steel column with 5% DC703/C20M on 100/120 mesh AW, DMCS Chromosorb 6, operated at 333 K. The N_2 carrier gas flow was 50 cm^3 min^{-1}, and a 3.0 cm^3 gas sample loop was used.

Propene, n-butane (and other > C_3 alkanes and alkenes) were analyzed using a 36 ft x 1/8 in stainless steel column of 10% 2,4-dimethylsulfolane (DMS) on C-22 firebrick (100/120 mesh) operated at 273 K. The N_2 carrier gas flow was 80 cm^3 min^{-1} and a 2.0 cm^3 gas sampling loop was used.

For all of these analytical systems, no preconcentration was necessary and flame ionization was employed in all uses.

It is recommended that these or equivalent gas chromatographic analysis techniques be used for methyl nitrite and the reference organics given in Section III.F.

B. Ozone Monitor

A chemiluminescence ozone analyzer is recommended for this protocol since the ozone analyzers utilizing ultraviolet absorption tend to respond not only to ozone but also to some chemicals which absorb radiation at 253.7 nm (e.g., the cresols [Atkinson et al. 1980]). This may include some of the OH radical or photolysis reaction products. In view of these potential problems, it is desirable to use a chemiluminescence O_3 monitor which utilizes the emission arising from the ozone-ethene reaction. The ozone analyzer used will have an optimum sampling rate specified by the manufacturer; any sampling rate less than ~2 liter min^{-1} is acceptable.

The ozone analyzer should be calibrated according to the manufacturer's specifications.

C. $NO-NO_2-NO_x$ Monitor

A chemiluminescence $NO-NO_2-NO_x$ monitor (using the ozone-nitric oxide reaction) is recommended for this protocol. The monitor should be calibrated according to the manufacturer's specifications.

D. Reaction Chamber and Fluorescent Lamp Irradiation Assembly

1. Reaction Chamber

A simple, yet totally adequate, reaction chamber consists of an ~75-liter FEP Teflon cylindrical reaction bag (FEP Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.), formed from three

pieces of 2 mil FEP Teflon (Figure 2). The two endpieces are ~45 cm in diameter with an ~45 cm wide, ~140 cm long piece forming the cylinder. Teflon is the preferred material for construction of the reaction chamber because of its general inertness to ozone, its lack of hydrocarbon off-gassing, and its good transmission characteristics in the 290-800 nm wavelength region.

2. Injection and Sampling Port

Prior to heat sealing the Teflon chamber sides, a port for injection of the reactants and for sampling must be fitted. This sampling and injection port should be constructed of TFE Teflon (TFE Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.) nuts and bolts with the appropriate Swagelok (Swagelok is a registered trade name of Crawford Fitting Company) stainless steel fittings.

Figure 3 shows the design of the sampling and injection port used in developing this protocol. The port consists of a 2 to 3 in long hollow bolt of Teflon (A), machined on the exterior surface with threads. The interior screw threads, hole (B), is 1/4 in in diameter and an ~8 in long 1/2 in o.d. Teflon tube is inserted as shown. Two Teflon nuts (D) then screw over the bolt (A), one on the inside of the bag, the other on the outside. Large Teflon washers (E) are placed between the Teflon bag and the nuts (D), thus enabling the nuts to be tightened without twisting or stretching the Teflon bag. The 1/4 in o.d. Teflon tube is connected outside the reaction bag to a glass-Teflon stopcock.

3. Heat Sealing

The Teflon port is first assembled on one of the ends of the chamber by tightening the Teflon nuts, as detailed above and as shown in Figures 2 and 3. The hole in the Teflon sheet through which the Teflon bolt (A) fits can be conveniently made using a cork borer. The sides of the resulting cylindrical bag are sealed together with a 500 watt thermal impulse heat sealer. It will probably be necessary to carry out preliminary testing of this heat sealing technique using scrap pieces of Teflon to obtain a heat setting that yields a strong seal.

4. Reaction Bag Cover

An opaque cover is necessary in order to avoid illumination of the chamber and hence photolysis of the reactant mixture prior to the

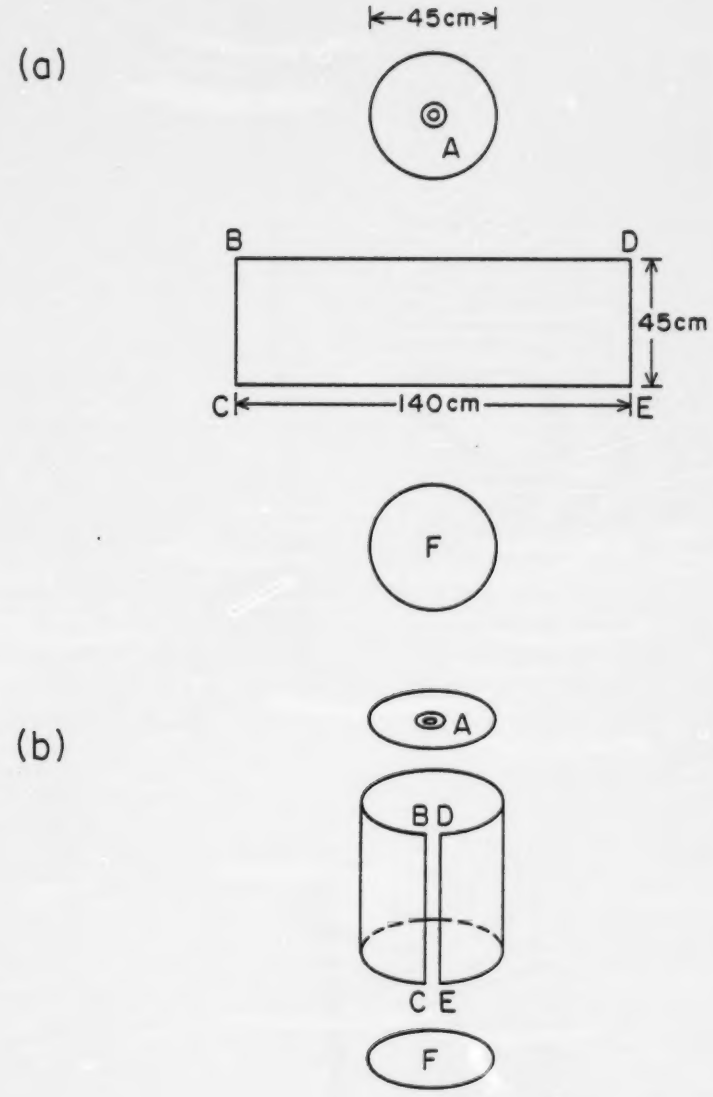
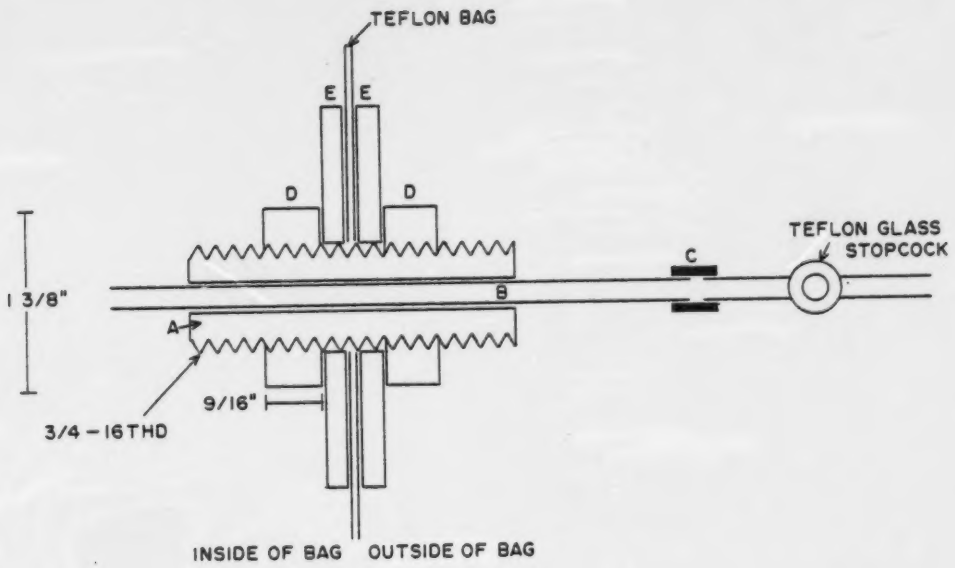


Figure 2. Construction of the Teflon Reaction Bag



A HOLLOW TEFLON BOLT
B 1/4" O.D. TEFLON TUBE INSERTED THROUGH 1/4" DIAMETER HOLE
C TYGON TUBING
D TEFLON NUTS
E TEFLON WASHERS

Figure 3. Injection and Sampling Port

beginning of the irradiation. A large opaque plastic sheet functions well.

5. Seal Reinforcement and Leak Testing

The heat sealed sides can be further protected from leaks by covering the heat-sealed seams with green Mylar tape (Scotch polyester-tape, catalog number 8403). After the bag is constructed it should be tested for obvious leakage by filling with pure air (ultra-high purity) to capacity (not excessively so as to split the seams) and then allowing the inflated bag, with the stopcock closed, to sit for one or two hours. After this period of time, the amount of deflation can be visually estimated. A certain amount of air will have permeated through the Teflon, but the bag should still be largely filled, and no obvious leaks should result from applying a small amount of pressure to the bag. The seams should be carefully examined for splits or tears, and, if any holes are found, they should be resealed (probably at a lower heat setting) and more Mylar tape applied to reinforce the seams.

6. Fluorescent Lamp Assembly

The fluorescent lamp assembly used in the development of this protocol is shown schematically in Figure 4. It consists of a circular array of 24 15-watt blacklights (GE F15T8-BL15) mounted in a cylindrical frame constructed out of aluminum. The lamps are arranged on three electrical circuits, eight lamps per circuit, with every third lamp being on a given circuit. This allows, in principle, the use of three differing light intensities, although the present protocol uses full light intensity. In the bottom of the chamber is a fan which circulates a large volume of air to minimize the amount of heating. A cylindrical wire mesh screen inside the lamp (Figure 4) keeps the reaction bag from contacting the lamps or the fan.

E. Reactor and Associated Apparatus for NO_2 Actinometry

The reactor cell for the determination of the NO_2 photolysis rate is a cylindrical quartz tube, 100 cm in length, 2.5 cm in diameter as shown in Figure 5. It is recommended that the first ~20 cm and last ~5-10 cm of this quartz tube be rendered opaque (with, for instance, black tape) to allow plug flow conditions to be maintained throughout the photolysis length. It is recommended that the NO_2 source be a commercially

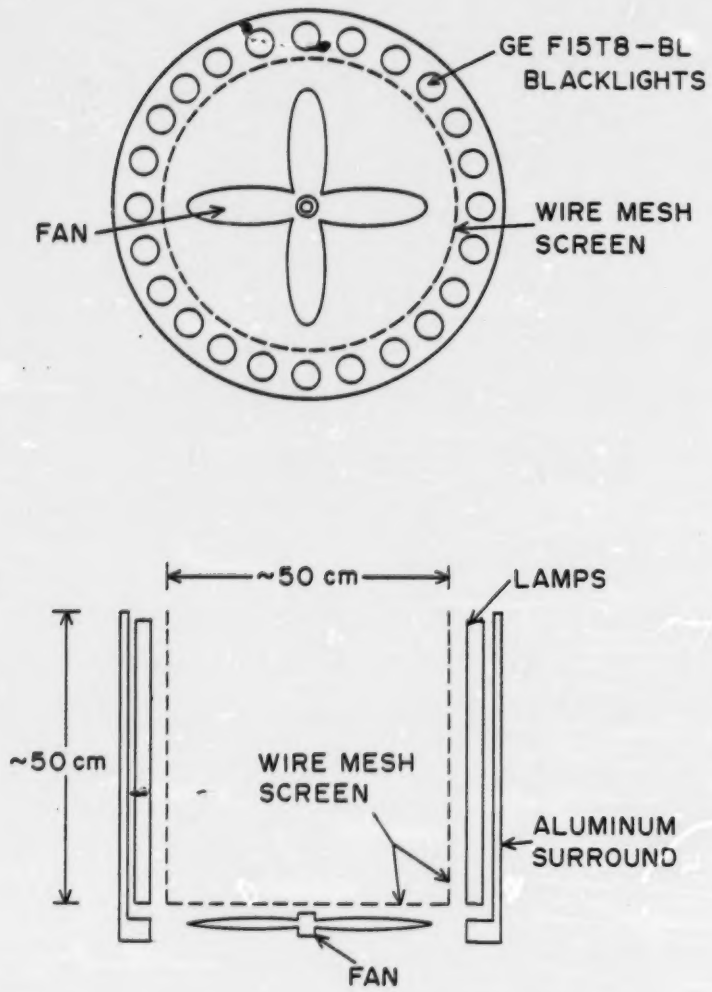
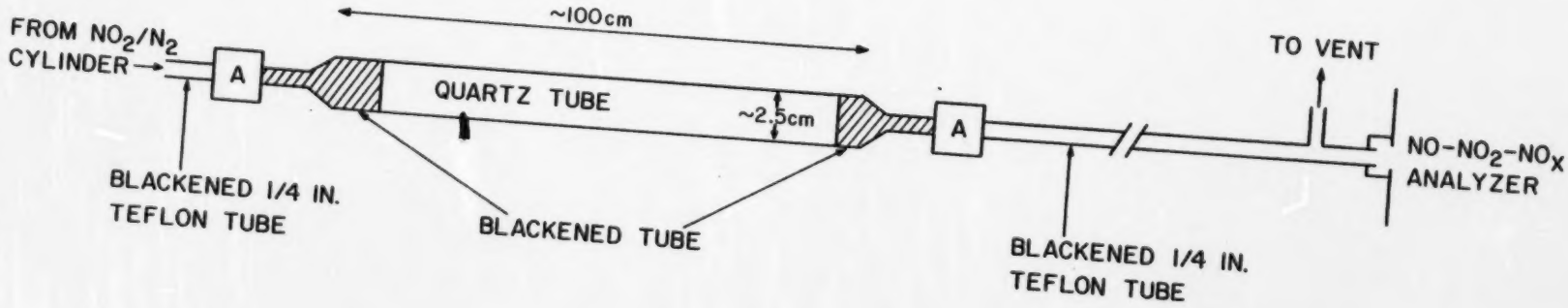


Figure 4. Fluorescent Lamp Assembly



A CAJON ULTRATORR FITTINGS

Figure 5. Schematic of NO_2 Actinometry Apparatus

calibrated cylinder of ~1.5 parts-per-million (ppm) of NO_2 in N_2. Connections to the cylinder and the NO-NO_2-NO_x monitor from the quartz tube are best made by blackened Teflon tubing (1/4 in o.d.).

F. Flowmeter

1. Range and Application

A rotameter (Matheson 604 flow meter or its equivalent) with a flow range of ~1 to 10 liter min^{-1} is required for the NO_2 actinometry, and is an effective means for controlling and monitoring the rate of fill of the reaction chamber. When not flushing a test compound into the chamber, the fill rate may be relatively rapid (i.e., ~7-10 liter min^{-1}). However, when a liquid needs to be introduced into the chamber, this is accomplished by flushing an ~1 liter bulb containing the compound of interest with pure air into the bag at a lower flow rate (i.e., ~3 liter min^{-1}) (at high flow rates the test compound may not fully vaporize before the bag is filled). A slower flow rate still may be useful for particularly nonvolatile compounds, though use of a heat gun will aid vaporization in these cases.

2. Calibration of the Rotameter

Rotameters are often accompanied by a manufacturer's calibration curve for air. Although this calibration curve, if available, could be used for the purposes of filling the reactant chamber, for NO_2 actinometry it is necessary to accurately determine the flow rate calibration curve for N_2. Flow rates should be determined at several (at least five) rotameter settings covering the flow rates to be used (i.e., 1-10 liter min^{-1}). At these flow rates, a wet test meter (Precision Scientific Model No. 63126 or equivalent) is preferable for measuring the flow rates, although a 1000 cm^3 or (preferably) a 2000 cm^3 bubble flowmeter can also be used. If neither a wet test meter nor a bubble flowmeter is available, a bubble flowmeter can be readily constructed by narrowing one end of a large glass tube (~5 cm diameter), as shown in Figure 6. Indelible lines can be drawn on the glass at intervals of 50 cm^3 upon adding water from a 50 cm^3 pipette and noting the water level after each successive addition of water (with, as shown in Figure 6, the zero line being above the narrow portion of the flowmeter) with the flowmeter in a vertical position. To the narrow end of the glass tube a glass "T" is attached by Tygon tubing,

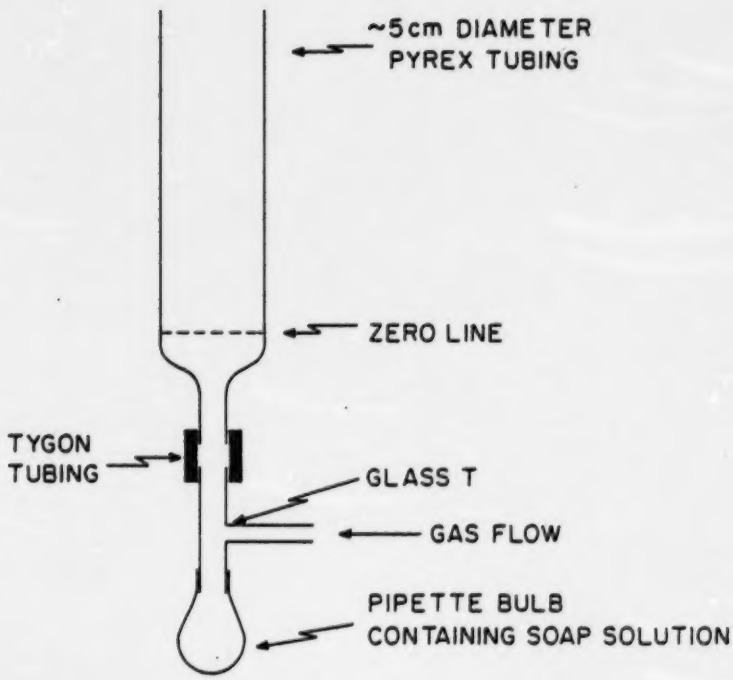


Figure 6. Design of a Bubble Flowmeter

and the lower arm is enclosed with a disposable pipette bulb. To the other arm of the "T" a Tygon tubing line which carries the gas is attached.

The N_2 or air should first be sent through the rotameter and its setting adjusted and noted. When using a wet test meter, measure the time, t, for a change of volume, V. For a bubble flowmeter, first squeeze the pipette bulb (containing soap solution, e.g., SNOOP [a registered trade name of Nupro Company]) to start a soap bubble and again measure the time, t, for the soap bubble to pass through a known volume, V, (the sidewalls of the bubble flowmeter should be wetted with soap solution so that bubbles will not break). For both types of flowmeters, at least three repeat readings should be taken at each rotameter setting. The volumes, V, should be such that the corresponding times, t, exceed 10 seconds. The flow rate, F, (in liter min^{-1}) is given by

$$F = \frac{V(cm^3) \times 60\ (sec\ min^{-1})}{t(sec) \times 1000\ (cm^3\ liter^{-1})} \qquad \text{(XIV)}$$

SECTION III

EXPERIMENTAL PROTOCOL

A. Experimental Procedure for the Determination of Rate Constants for Photolysis

1. Filling the Reaction Bag

Prior to each new experiment, the reaction bag should be completely emptied using a metal bellows pump whose exhaust is expelled into a hood. The bag should then be filled with pure air and pumped out again to remove any test compound or other reactants or products from the previous run. The desired amounts of the reactants (i.e., NO, the test compound and the reference organic) are then introduced (see below), and the reaction bag is then filled (i.e., visually filled but not excessively so as to cause undue stress on the seams) with ultra-zero air (for example, Liquid Carbonic, < 0.1 ppm hydrocarbons), using a flow rate in the region of ~7-10 liter min^{-1}, as monitored by the calibrated rotameter.

(a) Injection of Test Compound and Reference Organic

Concentrations of the test compound and reference organic used in the development of this protocol have been in the range of 0.5-2 ppm by volume. The following protocol details the introduction of a compound to yield a concentration of ~1 ppm in the reaction bag. The reaction bag must be kept in the dark during these injections.

1. Gaseous Compounds

If the test compound or reference organic is gaseous at room temperature, then the volume, V, of gaseous test compound needed is then given by:

$$V(cm^3) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{volume of reaction bag (liters)}] \qquad \text{(XV)}$$

Using the reaction bag described in this protocol, approximately 0.075 cm^3 of gas are required to yield a concentration of 1 ppm in the bag. With such a small volume of gas, 7.5 ml of gas is first transferred from a 10 ml all-glass gas syringe into a 100 ml all-glass gas syringe containing ~92.5 ml of pure air. For this transfer the two syringes are connected tip-to-tip by an ~0.4 in long Tygon tube, as shown in Figure 7. The

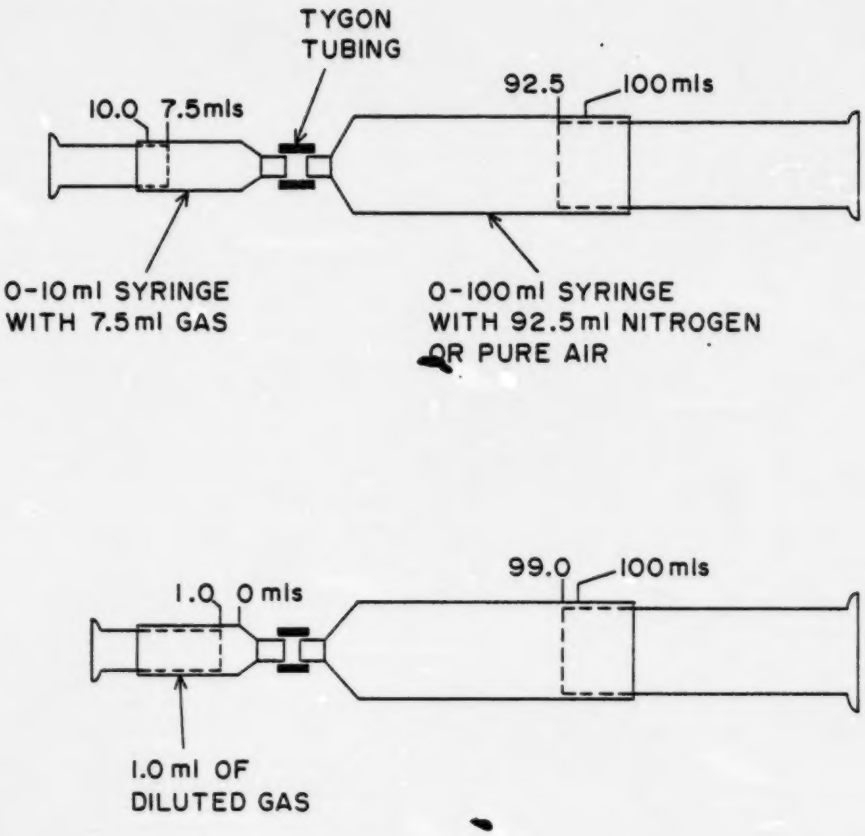


Figure 7. Syringe-to-Syringe Gas Transfer

syringes are pumped back and forth a few times to ensure mixing. From this 100 ml syringe, 1.00 ml is then taken into the 10 ml syringe and injected into an ~1-liter bulb modified as shown (Figure 8), which has been pre-flushed with pure air for $\geq$ 5 minutes. The contents of this closed 1-liter bulb are then flushed into the reaction bag with pure air.

2. Liquid Compound

If the test compound is a liquid, a different method of injection and of calculating the amount needed is necessary. For the reaction bag described in this protocol, approximately 0.5 µl of liquid will give a concentration appropriate for an experiment aimed at an initial concentration of ~1 ppm, since for the liquid case

$$V\ (\text{liters}) = 10^{-4} \times [\text{desired concentration (ppm)}] \times \frac{[\text{Volume of bag (liters)}] \times [\text{Molecular Weight (gm)}]}{[\text{Density (gm cm}^{-3})] \times 2.46} \qquad \text{(XVI)}$$

at room temperature.

It is necessary that the test compound be of the highest purity possible. Furthermore, any tendency of a compound to air oxidize or polymerize will lead to low volatility residues and hence errors when carrying out liquid injections. The compounds should, if such problems are known to be likely, be distilled by conventional means (i.e., vacuum distillation with liquid nitrogen trapping, vapor transfer from trap-to-trap at dry ice temperature, or by distillation at atmospheric or subatmospheric pressure).

Full safety precautions consistent with the known or unknown toxic, mutagenic or carcinogenic hazards of the test compounds must be taken (i.e., if the test compound is known to be hazardous or toxic, or if there is a reason to believe that it is, then handling should be carried out in a hood with disposable gloves, using a variable micropipette with disposable tips). Used gloves and tips should be disposed of according to safety regulations. If the toxicity of the compound is not a problem, a 10 µl capacity Hamilton liquid syringe may be used. It should be cleaned immediately after use by alternately drawing in and expelling methanol or

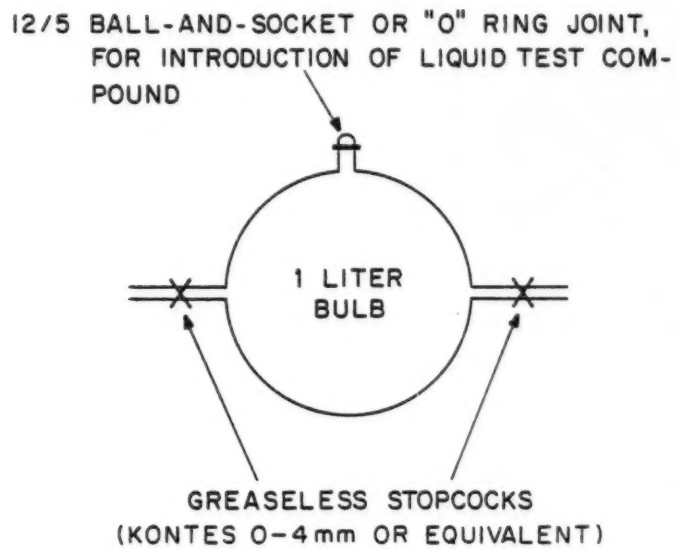

12/5 BALL-AND-SOCKET OR "O" RING JOINT, FOR INTRODUCTION OF LIQUID TEST COMPOUND
1 LITER BULB
GREASELESS STOPCOCKS
(KONTES 0-4 mm OR EQUIVALENT)

Figure 8. Design of Pyrex Bulb for Injection of Gaseous or Liquid Compounds

some other appropriate solvent five to ten times and then completely drying it by flowing dry nitrogen or pure air through the body of the syringe.

The calculated [see equation (XVI) above] amount of the liquid test compound is then injected into a 1-liter bulb, modified as shown in Figure 8, which has been preflushed with pure air into the hood for $\geq$ 5 minutes. The contents of the dosed 1-liter bulb are then flushed into the bag with pure air at a known flow rate, which should be ~3.5 liter min^{-1} for a more volatile liquid or less (~1-2 liter min^{-1}) for a nonvolatile liquid. Evaporation of the lower volatility liquids may be aided by gentle use of a heat gun to warm the 1-liter bulb (taking care not to pyrolyze the test compound).

(b) Injection of NO

Injection of NO is carried out in a manner similar to that for gaseous test compounds or reference organics, except that five times as much are needed for 5 ppm, and that nitrogen is used instead of pure air in the syringes and ~1-liter bulb, to avoid oxidation to NO_2.

2. Procedure for Photolysis Experiment

When the reactants have been injected in the reaction bag and mixed, the concentrations of the test compound and the reference organic are determined by gas chromatography (or by other applicable analytical techniques). For gas chromatography, samples are conveniently taken by a 100-ml all-glass, gas-tight syringe. While the data analysis does not require absolute concentrations, but only relative concentrations [equation (VI), Section I], the gas chromatograph(s) should preferably be calibrated for the test compound and reference organic. A minimum of three gas chromatographic samples should be analyzed prior to turning on the lamps. If the first two analyses agree to within ± 2%, then immediately after the third sample is taken from the reaction bag, the lamps can be turned on. If the first two analyses disagree by more than the variability determined by the precision of the analysis (typically ~2% for GC analyses of non-"sticky" compounds), then further samples should be taken until duplicate analyses do agree to within the analytical variability. In between gas chromatographic sampling, the $NO-NO_2-NO_x$ and O_3 analyzers should be sampling from the reaction bag, and their outputs displayed on stripchart recorders. Before beginning monitoring from the bag, these

analyzers should be allowed to warm up according to the manufacturer's specifications. Teflon sampling lines (1/4 in o.d.) should be used between the bag and the O_3 and $NO-NO_2-NO_x$ monitors in order to avoid losses experienced with, for example, Tygon or nylon tubing. The first three to five minutes of sampling should be neglected since initial flushing of the sample lines is needed.

When stable gas chromatographic readings have been established (see below), the full array of lamps are turned on, together with the cooling fan. Gas chromatographic samples are taken as often as possible. This is, of course, constrained by the retention times of the test compound and of the reference organic. Monitoring of O_3 and $NO-NO_2-NO_x$ should be carried out between sampling. Sampling for gas chromatographic analysis of the test compound and the reference organic must be carried out simultaneously.

With the protocol developed here, the irradiation should be carried out for a minimum of one hour.

B. Choice of Reference Organic

The reference organic used in these experiments must at a minimum have the following properties: (a) it should not photolyze, (b) it must have accurately known OH radical rate constants; (c) the rates of its reactions with O_3, $O(^3P)$, NO_3, etc., under the conditions of the photolysis rate determination must be negligible; (d) it must not undergo significant heterogeneous decay either in the dark (see Section I.B.2) or upon photolysis in Teflon bag reactors; and (e) it should be relatively easy to analyze with sufficient precision to accurately determine their decay rate with the analytical equipment available. Preferably, it should be analyzable using the same technique as the test compound (in the case of gas chromatography, if possible on the same instrument), and their OH radical rate constants should be similar (i.e., within a factor of two to three) to that for the test compound. In general, the best reference compounds in most respects are the simple alkanes, though for test compounds which react rapidly with OH radicals, an olefin might be preferable. However, if an olefin is employed, the importance of its reactions with O_3 in causing its consumption during an experiment must be checked using equation

(VII). Table 3 gives a list of recommended reference organics, together with their OH radical and O_3 reaction rate constants at room temperature.

C. Experimental Procedure for Measurement of the NO_2 Photolysis Rate

The rates of NO_2 photolysis, $k^{lab}_{NO_2}$, in the experimental system employed in the photolysis rate constant determinations described above, should be measured at a minimum immediately prior to and following the photolysis experiments.

The technique is as described by Zafonte et al. (1977). A known flow (measured by the rotameter) of the ~1.5 ppm NO_2 in N_2 mixture is flowed through the quartz tube and monitored by the NO-NO_2-NO_x monitor (Figure 3). This flow must be higher than the sampling requirements of the NO-NO_2-NO_x monitor, and ~3 liter min^{-1} is generally suitable. Readings of the NO and NO_2 concentrations are monitored until stable readings are obtained. The desired number of lamps (8, 16 or 24) in the fluorescent lamp assembly (nominally 24 for this protocol) are then turned on and the NO and NO_2 readings taken when stabilized. The lamps are then turned off and the background, i.e., cylinder, NO and NO_2 concentrations remeasured. The NO_2 in N_2 flowrate should then be remeasured to ensure no drift had occurred while the measurements were taken.

The NO_2 photolysis rate constant is calculated from the expression

$$k_{photolysis} = \frac{\Delta[NO]}{[NO_2]_{av}} \cdot \frac{F}{V} \cdot \frac{1}{\Phi} \cdot \frac{1}{T} \qquad \text{(XVII)}$$

where $\Delta[NO]$ is the change in the NO concentration on photolysis, $[NO_2]$ is the average NO_2 concentration within the photolysis cell, F is the flow velocity = (flowrate/internal cross-sectional area of the flow tube); V is the cell volume exposed to radiation, Φ is the quantum yield for NO production, and T is the transmission factor and represents the fraction of light transmitted by the reaction cell wall. As given by Zafonte et al. (1977), ϕ = 1.61, and for a cylindrical reaction cell T = 1. Hence

Table 3. List of Reference Organics for which Accurate OH Radical and O_3 Reaction Rate Constants are Available and which do not Photolyze

Organic	k(OH + organic) x 10^{12} (cm^3 $molecule^{-1}sec^{-1}$)[a]	k(O_3 + organic) x 10^{15} (cm^3 $molecule^{-1}sec^{-1}$)[a]
n-Butane	2.6[c]	b
Cyclohexane	7.6[c]	b
Ethene	8.5[c]	1.6[d]
Propene	25[c]	12[d]
Isoprene	96[c]	12[e]
2-Methyl-2-butene	87[c]	445[f]

[a]At 298 K.
[b]Negligible.
[c]Atkinson et al. (1982c) and references therein.
[d]Atkinson et al. (1982d) and references therein.
[e]Atkinson et al. (1982e).
[f]Mean of data from Japar et al. (1974) and Huie and Herron (1975).

$$k_{photolysis} = \frac{\Delta[NO]}{1.61[NO_2]_{av}} \quad \frac{F}{V} \qquad \text{(XVIII)}$$

From the reaction stoichiometry, $[NO_2]_{av}$ is given by

$$[NO_2]_{av} = [NO_2]_{measured} + \frac{\Delta[NO]}{1.61} \qquad \text{(XIX)}$$

where $[NO_2]_{measured}$ is the $[NO_2]$ as monitored by the $NO\text{-}NO_2\text{-}NO_x$ analyzer.

D. Determination of the Dark Decay Rate of the Test Organic

Separate experiments must be performed to determine whether dark decay of the test compound (i.e., reaction 3) is important; and, if so, to measure its rate constant, k_3. This is done by employing the same experimental procedure as described above in Section III.A, except that the lights are not turned on. Such experiments must be done using the same Teflon bag reaction as employed in the photolysis experiments, and should

be done before and after the photolysis. If non-negligible values of k_3 are found, additional experiments should be run to determine if the wall loss rate is reproducible. If it is not, or if k_3 appears to be anomolously high, the Teflon bag reactor should be replaced, and the k_3 determinations should be repeated using another reactor. In practice, for most reasonably volatile and stable organics, k_3 should be negligible.

E. Tests of the Experimental Technique and Potential Problem Areas

While in theory the present protocol is straightforward, yielding photolysis rate constants k_p, from equation (VI) and measured values of k_3, in practice (Atkinson et al. 1982a,b) the occurrence of first order wall losses of organics under irradiation can yield "apparent" photolysis rates which are spurious. This can, to some extent, be checked by irradiating two or more reference organics which do not photolyze in NO-air mixtures. The organics should be chosen to have widely differing OH radical rate constants (e.g., n-butane and isoprene). If values of $(k_p + k_3)$ which are significantly different from zero (i.e., outside of two standard deviations) are repeatedly found, then wall losses processes are suggested. In this case, a new Teflon reaction bag should be constructed and the experiments repeated.

In any case, such test irradiations should be carried out before and after experiments involving the test compound, and data for the test compound (i.e., the experimental protocol described in Section III.A) should be obtained employing more than one reaction bag to check for the possible significance of light induced, heterogeneous loss of the test compound (see Section I.B.2). In addition, to check for possible unsuspected homogeneous bimolecular loss process of test compounds whose chemistry in NO_x-air irradiations is uncertain, the experimental protocol should be repeated at different initial reactant ratios. Only if the test irradiations show no wall loss or other problems and the photolysis rate data for the test organic from two or more reaction bags and initial reactant concentrations agree can any confidence be placed in the desired test organic photolysis rate.

F. Data Analysis

The results of the NO-test compound-reference organic-air irradiations are analyzed as discussed in Section I A 1. Specifically, based on equation (VI), the experimental quantities

$$\frac{1}{(t-t_o)} \ln \frac{[\text{test compound}]_{t_o}}{[\text{test compound}]_t}$$

are plotted against

$$\frac{1}{(t-t_o)} \ln \frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t}$$

and the intercept should be $(k_p + k_3)$, the sum of the photolysis rate and the heterogeneous decay rate, and the slope should be k_2/k_4, the ratio of the OH radical rate constants for the test compound and the reference organic. If the test compound or the reference organic react with a non-negligible rate with O_3, then for each time interval (t_1, t_2) equation (VII) should be applied to determine the estimated extent of consumption of each compound with O_3. Points where the O_3 reaction is > 10% for either the test compound or the reference organic should not be used in the subsequent data analysis.

The plot based on equation (VI), with the points where O_3 reaction is > 10% excluded, should be linear, and a linear least-squares regression calculation can be done to determine $(k_p + k_3)$ and k_2/k_4. If the plot is non-linear, then it must be concluded that there is another sink for the test compound other than photolysis or reaction with OH radicals which is important in these irradiations; and the experiment must be considered to be unsuccessful. However, if the curvature only occurs around the latter stages of the run, when O_3 and thus NO_3 concentrations are at their highest, and is in the direction of increasing rates of consumption of the test compound relative to that of the reference organic, then the curvature might be caused by a rapid reaction between the test compound and NO_3; in that case, the curvature should be eliminated by experiments performed at higher NO levels. The experiment must also be considered to be unsuccessful if the slope of the plot is not equal, to

within experimental uncertainties, to the ratio of OH radical rate constants for the test and reference compounds. In any case, the $(k_p + k_3)$ values so derived must be considered to be strictly upper limits to the true values.

Alternatively, since the rate constant ratio k_2/k_4 will be known prior to this protocol being carried out, values of $(k_p + k_3)$ may be calculated from the experimental values of $(t-t_o)^{-1}\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ and $(t-t_o)\ln([\text{reference organics}]_{t_o}/[\text{reference organic}]_t)$ using equation (VI) for each set of data points.

The results of the dark experiments, performed to measure k_3, the dark decay rate of the test compound in the reaction, are analyzed somewhat differently. Since reaction (3) should be the only sink for the test compound, a plot of $\ln([\text{test compound}]_{t_o}/[\text{test compound}]_t)$ against t should yield a straight line with a slope of k_3. The uncertainty in k_3, either as a result of the scatter or the data in single experiments, or as a result of scatter of results of different experiments (whichever is greater) should be noted. If there is no apparent dark decay, its upper limit rate should be noted.

The values of k_3 so obtained are then subtracted from the intercept of the plot of equation (VI) to obtain k_p^{lab}, the upper limit photolysis rate of the test compound. If the measured value of k_3 is within experimental uncertainty of $(k_p + k_3)$, then the standard deviations of the measurements of k_3 or $(k_p + k_3)$, and the estimated experimental uncertainties, are used to obtain an estimate of the upper limit of k_p^{lab}. This value, along with the measured values of $k_{NO_2}^{lab}$ obtained using the same light source at the same intensity as used in the NO-organic-air irradiations, and tabulated values of $k_{NO_2}^{trop}$ are then used in Equation (XIII) to obtain an estimate to the value of k_p^{trop}. It should be noted, however, that because of the uncertainties introduced by the fact that the spectral distribution of the light source is not the same as that of tropospheric sunlight (see Section I.B.3), this estimated value of to k_p^{trop} may possibly be different than the true value.

Since the absorbtion coefficients of the test organic should have been measured (Pitts et al. 1981b) prior to performing this protocol for measuring the photolysis rates, it should be possible to compare maximum photolysis rates, calculated using equation (III), with the experimentally

determined values. This can be done at a minimum for k_p^{trop}, since tabulated values of $J_{\Delta\lambda}$ for tropospheric conditions are available (Hendry and Kenley 1979, Peterson 1976, Pitts et al. 1981b). However, a more direct test of the validity of the experimental determination would be to calculate k_p^{lab} (max) from the spectral distribution of the laboratory photolysis system (e.g., the blacklights). The techniques for measuring spectral distributions of laboratory light sources is beyond the scope of this document; but, if the 15-watt, GE FT15T8-BL15 blacklights are employed, the spectral distribution will probably not be too different from that shown in Figure 1. k_p^{lab} (max) can be calculated from the relative spectral distributions of the laboratory system, $J_{\Delta\lambda}$(rel), and the measured value of $k_{NO_2}^{lab}$ using the equation:

$$k_p^{lab}(max) = \frac{\Sigma_\lambda J_{\Delta\lambda}(rel)\ \sigma_\lambda}{\Sigma_\lambda J_{\Delta\lambda}(rel)\ \sigma_\lambda^{NO_2}\ \phi_\lambda^{NO_2}} \cdot k_{NO_2}^{lab} \qquad (XX)$$

where σ_λ are the absorption coefficients for the test compound, and $\sigma_\lambda^{NO_2}$ and $\phi_\lambda^{NO_2}$ are the known absorption coefficients and quantum yields for NO_2 photolysis (Atkinson and Lloyd 1983). If the experimental k_p^{lab} or k_p^{trop} values are higher than the calculated maximum values, they must be considered to be invalid, and the value calculated from the absorption coefficients must be used as the upper limit photolysis rates for purposes of estimating tropospheric lifetimes.

G. Information to be Reported

A report of the results should include, for each test compound, the following:

(a) The compound's name, formula and physical properties (boiling and melting points), absorption spectrum in the λ = 290-800 nm range, and OH radical and O_3 reaction rate constants.

(b) The chemical's physical form used during injection (gas or liquid at room temperature), method of purification and purity (including analysis of impurities).

(c) The temperature during each run.

(d) The lamps used, their intensity (in terms of the NO_2 photolysis rate in N_2) and a spectrum of these lamps.

(e) The name and formula for the reference organic used and the rate constant k_2 used in the data analysis.

(f) The initial concentrations of the reference organics and test compound and NO in all irradiation experiments and dark decay determinations.

(g) The data obtained (i.e., the concentrations of the reference organic and test compound prior to and during irradiation, and the values of $(t-t_o)^{-1}\ln$ ([reference organic]$_{t_o}$/[reference organic]$_t$) and $(t-t_o)^{-1}\ln$ ([test compound]$_{t_o}$/[test compound]$_t$) in the irradiation experiments, and the measured values of the test compound and the times of the measurements for the dark decay experiments.

(h) The data obtained from any associated bag characterization experiments.

(i) If more than one reactor was employed in the reported experiment, it should be identified along with the results.

(j) The values of $k_3 + k_p^{lab}$ and k_3 and their error limits as determined from the analysis of the data from the appropriate experiments, and the resulting values (or upper limit) of k_p^{lab} and its error limits.

(k) The calculated value of k_p^{trop}, and the value of $k_{NO_2}^{trop}$ upon which it is based, and an indication of the source of the $k_{NO_2}^{trop}$ value employed.

(l) The calculated value of $k_p^{trop}(max)$ from the absorption coefficients of the test compound under the conditions used in (k), above, and an indication of the source of the $J_{\Delta\lambda}$ values used.

REFERENCES

Atkinson, R., K. R. Darnall, A. C. Lloyd, A. M. Winer and J. N. Pitts, Jr., 1979. Kinetics and mechanisms of the reaction of the hydroxyl radical with organic compounds in the gas phase. Adv. Photochem., 11, 375.

Atkinson, R., W. P. L. Carter, K. R. Darnall, A. M. Winer and J. N. Pitts, Jr., 1980. A smog chamber and modeling study of the gas phase NO_x-air photooxidation of toluene and the cresols. Int. J. Chem. Kinet., 12, 779.

Atkinson, R. and A. C. Lloyd, 1983. Evaluation of kinetic and mechanistic data for modeling of photochemical smog. J. Phys. Chem., Ref. Data, in press.

Atkinson, R., S. M. Aschmann, W. P. L. Carter and J. N. Pitts, Jr., 1982a. Rate constants for the gas-phase reaction of OH radicals with a series of ketones at 299 ± 2 K. Int. J. Chem. Kinet., 14, 839.

Atkinson, R., S. M. Aschmann, W. P. L. Carter and A. M. Winer, 1982b. Kinetics of the gas-phase reactions of OH radicals with alkyl nitrates at 299 ± 2 K. Int. J. Chem. Kinet., 14, 919.

Atkinson, R., S. M. Aschmann, A. M. Winer and J. N. Pitts, Jr., 1982c. Rate constants for the reaction of OH radicals with a series of alkanes and alkenes at 299 ± 2 K. Int. J. Chem. Kinet., 14, 507.

Atkinson, R., S. M. Aschmann, D. R. Fitz, A. M. Winer and J. N. Pitts, Jr., 1982d. Rate constants for the gas phase reactions of O_3 with selected organics at 296 K. Int. J. Chem. Kinet., 14, 13.

Atkinson, R., A. M. Winer and J. N. Pitts, Jr., 1982e. Rate constants for the gas phase reactions of O_3 with the natural hydrocarbons isoprene and α- and β-pinene. Atmos. Environ., 16, 1017.

Benson, S. W., 1976. Thermochemical Kinetics. 2nd Ed., Wiley-Interscience, New York, NY.

Calvert, J. G. and J. N. Pitts, Jr., 1966. Photochemistry. John Wiley & Sons, Inc., New York, NY.

Demerjian, K. L., K. L. Schere and J. T. Peterson, 1980. Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants for atmospheric species in the lower troposphere. Adv. Environ. Sci. Technol., 10, 369.

Finlayson-Pitts, B. J. and J. N. Pitts, Jr., 1977. The chemical basis of air quality: Kinetics and mechanisms of photochemical air pollution and application to control strategies. Adv. Environ. Sci. Technol., 7, 75.

Hendry, D. G. and R. A. Kenley, 1979. Atmospheric Reaction Products of Organic Compunds. EPA-500/12-79-001, June.

Herron, J. T., R. E. Huie and J. A. Hodgeson, 1979. Eds., "Chemical Kinetic Data Needs for Modeling the Lower Troposphere," National Bureau of Standards Special Publication 557, August.

Huie, R. E. and J. T. Herron, 1975. Temperature dependence of the rate constants for reactions of ozone with some olefins. Int. J. Chem. Kinet. Symp., 1, 165.

Japar, S. M., C. H. Wu and H. Niki, 1974. Rate constants for the reaction of ozone with olefins in the gas phase. J. Phys. Chem., 78, 2318.

Lindley, C. R. C., 1979. Ph.D. Thesis, The Ohio State University, Columbus, Ohio.

Peterson, J. T., 1976. Calculated Actinic Fluxes (290-700 nm) for Air Pollution Photochemistry Applications. EPA-600/4-76-025, June.

Pitts, J. N., Jr., K. Darnall, W. P. L. Carter, A. M. Winer and R. Atkinson, 1979. Mechanisms of Photochemical Reactions in Urban Air. EPA-600/3-79-110, November.

Pitts, J. N., Jr., A. M. Winer, D. R. Fitz, S. M. Aschmann and R. Atkinson, 1981a. Experimental Protocol for Determining Ozone Reaction Rate Constants. EPA-600/3-81-024, May.

Pitts, J. N., Jr., A. M. Winer, D. R. Fitz, A. K. Knudsen and R. Atkinson, 1981b. Experimental Protocol for Determining Absorption Cross Sections of Organic Compounds. EPA-600/3-81-051, December.

Pitts, J. N., Jr., A. M. Winer, S. M. Aschmann, W. P. L. Carter and R. Atkinson, 1982. Experimental Protocol for Determining Hydroxyl Radical Reaction Rate Constants. EPA-600/3-82-038, October.

Plum, C., E. Sanhueza, R. Atkinson, W. P. L. Carter and J. N. Pitts, Jr., 1983. Environ. Sci. Technol., in press.

Zafonte, L., R. L. Rieger and J. R. Holmes, 1977. Nitrogen dioxide photolysis in the Los Angeles atmosphere. Environ. Sci. Technol., 11, 483.